# Comparison of spray retention on synthetic superhydrophobic surface with retention on outdoor grown wheat leaves

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**Summary**

A method has been designed to test the retention of drops generated by a moving agricultural nozzle using high speed imaging both on synthetic and leaf surfaces. The method allows a precise investigation of spray retention by a characterisation of impact speed, drop diameter and impact behaviour. The paper presents a comparison of the spray behaviour on the synthetic surface with the behaviour on outdoor grown wheat leaves fixed on a microscope slide. Target surfaces were horizontal. A range of surface tension was tested using the tank-mix adjuvant Break-Thru S240 at different concentrations in distilled water. Results show the relevance of a synthetic surface for use as reference for the assessment of spray application efficiency. The drop behaviour on the superhydrophobic slide was representative of difficult-to-wet leaves surfaces. The reference surface avoids the natural variability of leaves and is therefore more suited to conduct comparative assessment of formulation retention performance.

**Key words**: Spray retention, drop, leaf, outdoor wheat, superhydrophobic surface, wettability, high speed imaging

## Introduction

Spray application efficiency depends on the pesticide application method as well as spray liquid properties. For environmental and economic reasons, the global trend is to reduce the pesticide application rate of the few approved active substances. Under these constraints, one of the challenges is to improve the efficiency of the application process.

This process can be divided into four individual stages: deposition, retention, uptake and translocation (Zabkiewicz, 2007). The spray retention defined as the quantity retained on the plant is usually measured as the quantity deposited on the whole plant (Butler Ellis *et al*., 2004). This method offers a precise quantification of the application process efficiency but fails to identify the contribution of individual parameters involved. Indeed, retention is influenced by the nozzle type, pressure and formulation and also by growth stage, plant canopy and environmental conditions. As a result, application process is governed by physical parameters of drop speed and diameter, spray liquid surface tension and viscosity, leaf angle, canopy density and surface wettability.

Plants exhibit various degrees of wettability from very-easy to very-difficult-to-wet, depending on species and growth stages (Gaskin *et al*., 2005). It is well established that difficult-to-wet species such as wheat or black-grass are the most challenging target for efficient pesticide application.

Superhydrophobicity appears on hydrophobic materials when the apparent contact angle is enhanced by the small scale roughness of surface that dramatically increased their specific surface. In plants, superhydrophobicity originates from cuticle pattern, waxes and hairs on the leaf surface.

Two models are classically used to describe the wetting of such surfaces named Wenzel and Cassie-Baxter regime (Zu *et al*., 2010). The Wenzel non-composite regime, often referred as pinning, is characterised by the sticking of the liquid which is anchored in the surface cavities. In the Cassie-Baxter composite regime, the liquid stands on the pillars of the surface and some air is trapped beneath the drop in the valleys of the structure. The liquid can be easily removed from the surface. The height and distance between the pillars is a critical parameter to keep the drop in a Cassie-Baxter regime. One classical parameter to quantify the surface roughness is the Wenzel roughness defined as the ratio of the real and the projected planar surface areas (Rioboo *et al*., 2008).

As a result of these regimes, different outcomes during drop impact have been identified on superhydrophobic materials as a function of drop size and velocity and surface roughness (Fig. 1). For small Wenzel roughness, a drop of low kinetic energy is deposited in a Wenzel state. By gradually increasing its kinetic energy, the drop is fragmented. A part of the drop sticks at the impact point while the rest leaves the surface. As a function of the impact energy, one drop can bounce, in what is referred as partial rebound, or several satellite drops are shattered, in what is referred pinning fragmentation. For intermediate Wenzel roughness, slowly impacting drops adhere in a Cassie-Baxter regime. With increasing speed, the drop completely bounces, in what is only observed on superhydrophobic surface (Richard & Quere, 2000). For even higher speeds, when the impact pressure is large enough, the liquid can penetrate into the cavities of the surface modifying the wettability regime from Cassie-Baxter to Wenzel. As a consequence, sticking, partial rebound or pinning fragmentation can be observed. Finally, for high Wenzel roughness, a drop can, as a function of speed, either adhere in a Cassie-Baxter regime, rebound or completely splash. In this last case, all the liquid is shattered into numerous satellite drops.

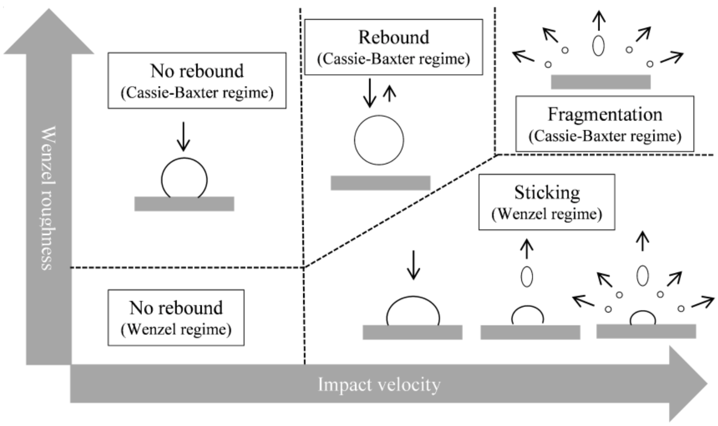



Fig. 1. Phase diagram of drop impact on a superhydrophobic surface as a function of drop velocity and surface roughness (Rioboo *et al*., 2008).

The outcome of a drop impact is classically predicted using dimensional analysis which establishes the relationship between variables involved in the retention process (Lake & Marchant, 1983). The relevant dimensionless parameter governing the drop-surface interaction is the dimensionless Weber number ($We = \rho v^2 d / \sigma$) representing the ratio between the drop kinetic energy and the liquid surface tension, where $\rho$ is liquid density, $v$ is the velocity, $d$ is the drop diameter and $\sigma$ is the liquid surface tension. Based on its physical meaning and the integration of several parameters, a constant Weber number can be used to quantify the transitions between impacts (Rioboo *et al*., 2008).

To identify such transitions, the retention of individual drops has been studied using imaging devices and drop generators (Reichard *et al*., 1998). This allows a precise determination of the drop behaviour during impact as a function of physical parameters but has the drawback of the limited drop speed of on-demand generators comparatively to agricultural nozzles (Forster *et al*., 2005).

To overcome these limitations, a method was devised to study impaction of agricultural nozzles drops and used to compare spray additive effects on a synthetic superhydrophobic surface (Massinon & Lebeau, 2012). The present paper compares the spray retention on the homogeneous synthetic surface with the behaviour on outdoor grown wheat leaves fixed on a horizontal microscope slide. The aim is to highlight the similarities and discrepancies between these targets and determine if synthetic surface can be used as a model surface of the actual leaf to highlight the effects of practical choices or guide formulation manufacturers in their developments. Furthermore, it aims to determine if the physical models developed to understand the behaviour of synthetic surfaces can be transposed to real leaves. Different concentrations of a surfactant are sprayed in order to show the influence on retention.

## Materials and Methods

### *Dynamic spray application bench*

A dynamic spray application bench was used to study spray retention (Fig. 2). Drops are generated by a single flat-fan Teejet XR11003VK nozzle mounted on a height-adjustable boom sprayer. A linear displacement stage actuated by a servomotor moved the nozzle at a forward speed of 2 m $s^{-1}$. A single pass of the nozzle 50 cm above the target was performed. Drop impact event was recorded at 20000 frame per second (Y4 CMOS, Integrated Design Tools) using LED backlighting (19LED Constellation, Integrated Design Tools). Camera, lighting and target surface are aligned horizontally. In this configuration, drop size and velocity can be measured just before impact. A linear translation stage is used to adjust the target position in the camera focalisation plane. A horizontal slit plate, aligned to the focalisation plane, is placed one centimetre above the surface to select drops that are in the focalisation plane. The nozzle is connected to a classical hydraulic supply system. Pressure was set to 0.3 MPa for all experiments.

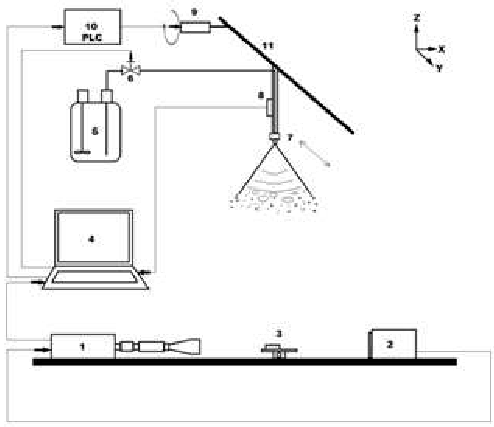



Fig. 2. Dynamic test bench, (1) Camera; (2) Lighting; (3) Target surface on linear stage; (4) Computer; (5) Pressurised tank; (6) Solenoid valve; (7) Nozzle; (8) Pressure gage; (9) Servomotor; (10) Programmable controller; (11) Linear stage.

Size and velocity of drops are determined by image analysis using dedicated software developed in Matlab® (The MathWorks Company, Massachusetts, USA). Impact types are determined by the user and boundaries between impact classes are characterized by a constant Weber number. The latter was determined by finding the intersection between Weber number probability density distributions of the different impact outcomes. Volumetric proportions within each class are calculated.

### *Sprayed formulations*

A trisiloxane tank-mix adjuvant (Break-Thru S240, Evonik Industries AG) was sprayed on target surfaces at 3 concentrations in distilled water: 0.025, 0.05 and 0.1% V/V. Distilled water was tested as a reference. At least five replicates were conducted for each formulation/surface combination. Static surface tension was measured with the sessile drop method in five replicates (Table 1). The latter was used to calculate Weber numbers for transitions between impact types.

### *Horizontal target surfaces*

The superhydrophobic surface was a Teflon coated microscope slide (Thermo Scientific, part number X2XES2013BMNZ). Leaf surfaces are excised from outdoor grown wheat (*Triticum aestivum* L. cv Julius) and fixed on a microscope slide with a double-sided tape (Fig. 3). Manipulations of leaf surfaces are made with care using latex gloves to avoid modifications of surface properties. The tip and base of the leaves were tested. Results have been merged to be representative of the whole leaf.

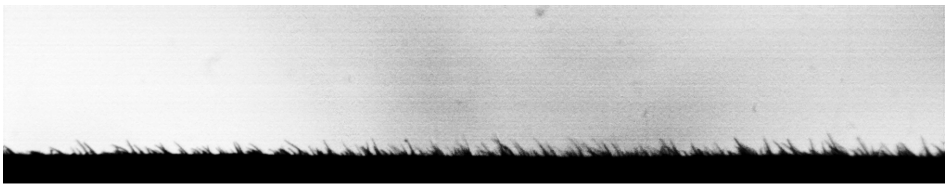


Fig. 3. Picture of the tip of a winter wheat leaf showing a dense pilosity. Picture size is 10 mm × 2 mm.

The static contact angle of distilled water on Teflon slide was 169°. Contact angle measured perpendicularly from leaf axis was 161°. The value was 150° parallel to axis of the leaf. Measurements of static contact angles for the surfactant were impossible because of its rapid spreading. It appears that the contact angle of the Teflon slide was similar to that of wheat when perpendicular to the leaf axis but lower in the parallel direction. The anisotropic surface of the wheat influences the impact outcome in that the satellite drops being directed preferentially along the main axis during their spreading.

## Results

### *Distilled water*

Fig. 4 presents spray experiment results as a function of drop diameter and the impact velocity on a log-log scale graph for distilled water. Each symbol represents the drop impact outcome. Most of the drops of the spray are scattered along a sigmoid curve because of the deceleration from initial speed. For diameters below 200 µm, drops impact the surface near their terminal velocity after covering the 50 cm height distance. For diameters above 200 µm, drops are impacting at a higher velocity because of their high Stokes relaxation time.

On the Teflon slide (Fig. 4a), the different outcomes are sharply separated by Weber boundaries. Outcome distributions are characteristic of the theoretical high Wenzel roughness behaviour. Only a few drops were deposited in the Cassie-Baxter regime and most drops bounced. Some drops came back in the field of view and undergo a secondary impact. The most energetic drops splash at impact.

At first glance, the behaviour on the wheat leaves presents a much wider variability (Fig. 4b). However, clear similarities appear when examined more closely. Rebound still occurs for a wide range of Weber numbers but deposits appear probably because of the natural surface heterogeneity. This may also be related to dirt as it is well established that superhydrophobicity is very sensitive to any soiling of the surface. Indeed retention tests showed a clear difference between outdoor and greenhouse grown plants (Butler Ellis *et al*., 2004). The splashing boundary is quite similar, what is consistent is the fact that this boundary is known to be less related to the surface properties than to the fluid rheology (Vander Wal *et al*., 2006).

*Surfactant formulations*

Fig. 5 presents the effect of different surfactant concentrations on both surfaces. On the Teflon slide (Fig. 5a,c,e), increasing the surfactant concentration leads progressively to the vanishing of the rebound events. Complete extinction is observed for the highest concentration tested, 0.1% surfactant solution, that corresponds to the manufacturer recommendation. The Weber number characterising the adhesion/rebound transition increases accordingly. It can also be observed that at 0,025% the remaining rebound events were surrounded by adhesions. The high Weber number adhesion probably corresponds to the pinning caused by a Cassie-Baxter to Wenzel transition resulting from the impact energy and surfactant effect. Splashing occurred at a slightly lower Weber number with increasing surfactant concentration. On the wheat leaf (Fig. 5b, d, f), a higher variability of the outcome of impacts was observed but rebound disappeared for lower Weber numbers. The observed variability was not found related on the location of the impact on the leaf but seems related to variability between leaves. It is suspected that it originates from fouling differences between outdoor grown leaves. On both surfaces, splashing is replaced by a pinning fragmentation at the higher surfactant concentration.

Table 1: *Static surface tension (five replicates, CAM200, KSV) and volumetric percentages in impact classes for each formulation*

| | | Distilled water | BT 0,025% | BT 0,05% | BT 0,1% |
|---|---|---|---|---|---|
| Static surface tension ($N\ m^{-1}$) | | 0,072 | 0,023 | 0,022 | 0,022 |
| Teflon slide | %vol adh. | 4,26 | 28,83 | 38,68 | 52,63 |
| | %vol reb. | 70,12 | 12,27 | 2,58 | / |
| | %vol frag. | 25,62 | 58,9 | 58,74 | 47,37 |
| Wheat leaf | %vol adh. | 25,06 | 19,45 | 26,85 | 38,6 |
| | %vol reb. | 27,32 | 19,91 | 13,77 | 12,6 |
| | %vol frag. | 47,62 | 60,64 | 59,38 | 48,8 |

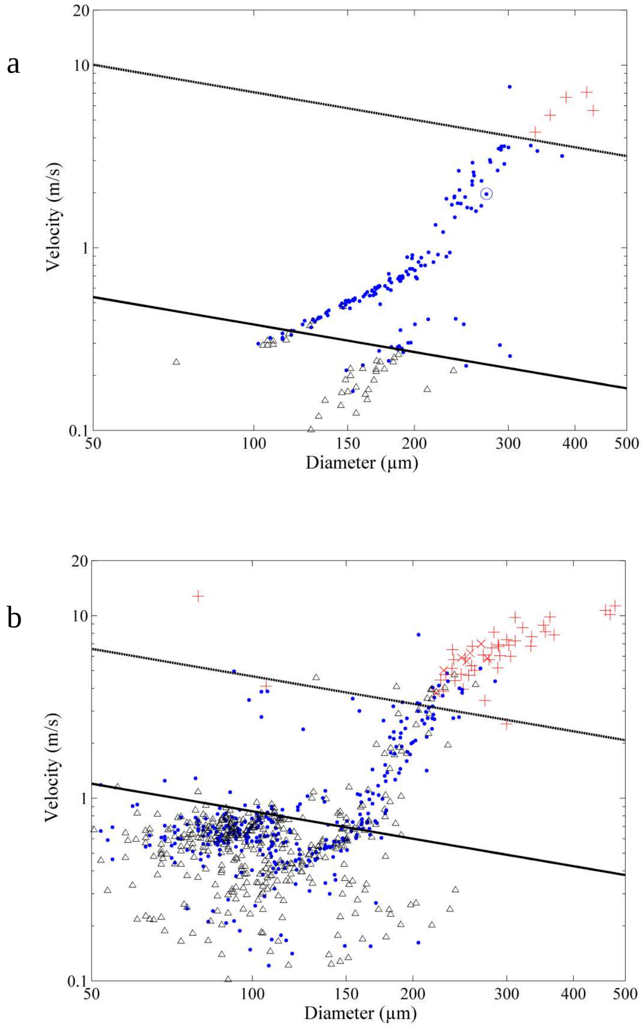
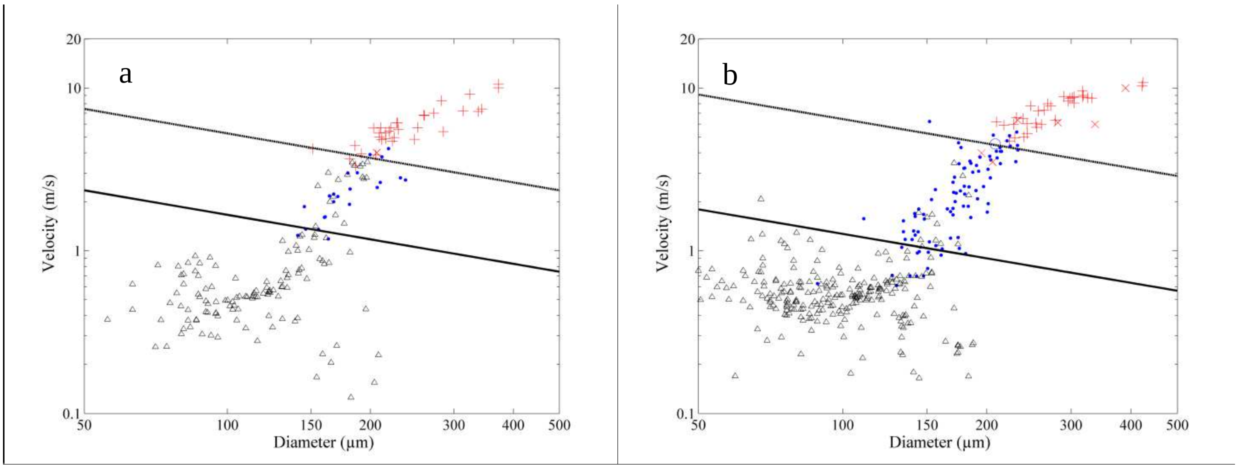



Fig. 4. Outcomes after drop impact for distilled water on Teflon slide (a) and winter wheat leaf (b). Δ adhesion, ● rebound, ○ pinning rebound, × pinning fragmentation and + complete fragmentation. ─ Weber number of transition between adhesion and rebound (a:0.2; b:1) , -- Weber number of transition between rebound and fragmentation (a: 70; b:30).



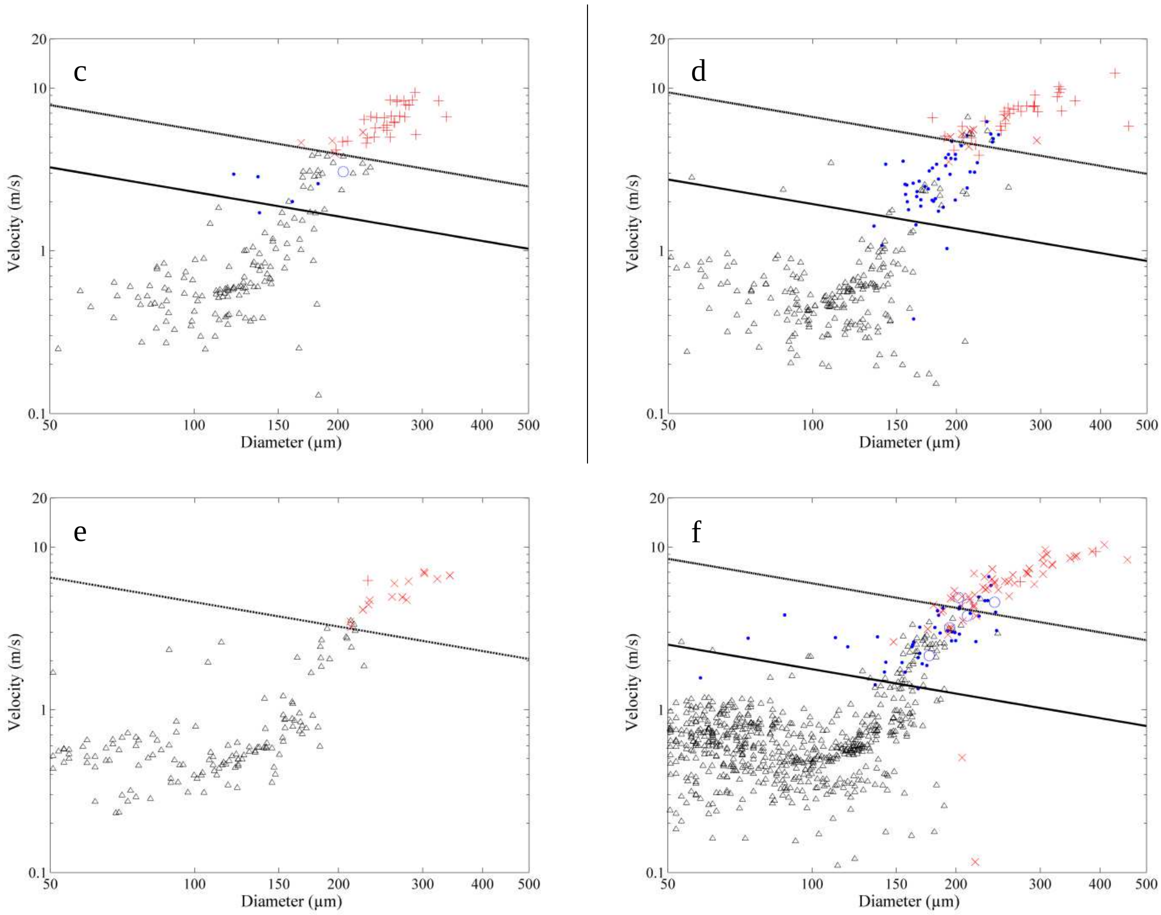



Fig. 5. Outcomes after drop impact. (a,c,e) Teflon slide, (b, d, f) Wheat leaf, (a-b) 0.025% surfactant, (c–d) 0.05% surfactant and (e–f) 0.1% surfactant. Δ adhesion, • rebound, ○ pinning rebound, × pinning fragmentation and + complete fragmentation – Weber number of transition between adhesion and rebound (a–f: 12; 6; 24; 17; /, 15) , -- Weber number of transition between rebound and fragmentation (a–f:120; 180; 140; 200; /; 170 ). ····Weber number of transitionbetween adhesion and fragmentation (e: 100).

## Discussion

Results clearly show high similarities between drop behaviour during impact on the synthetic superhydrophobic surface and wheat leaves. The possible different outcomes were observed on both surfaces and were consistent with recent theoretical developments on superhydrophobic materials. The use of synthetic surface is more suited to identify and quantify precisely the effect of the surfactant because of lower variability.

Future work will focus on different surfactants presenting various dynamic surface tensions (DST) as the time scale of drop deformation during impact is very low (< 5 ms). As a result, attention must be paid to the value of DST to be used to accurately predict impact outcome (Crooks *et al.*, 2001, Mourougou-Candoni *et al.*, 1997). Other rheological properties will also be investigated as the use of non-Newtonian fluids is a promising way to reduce fragmentation. It was observed that wheat leaves present an anisotropic surface that influences the impact outcome, satellite drops being directed preferentially along the main axis. Consequences on retention should be studied further. Moreover leaf angle effects should also be studied further. Last but not least, fouling is suspected to reduce drastically rebound in practical application on outdoor grown leaves, what was observed in previous retention studies (Butler Ellis *et al.*, 2004).

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